

2

AD-A207 140

DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. CLASSIFICATION AUTHORITY		1b. RESTRICTIVE MARKINGS													
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.													
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR-89-0503													
6a. NAME OF PERFORMING ORGANIZATION State University of New York at Buffalo	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR													
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Buffalo, New York 14214		7b. ADDRESS (City, State, and ZIP Code) BLDG 410 BAFB DC 20332-6448													
8a. NAME OF FUNDING / SPONSORING ORGANIZATION AFOSR	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-79-C-0229													
8c. ADDRESS (City, State, and ZIP Code) BLDG 410 BAFB DC 20332-6448		10. SOURCE OF FUNDING NUMBERS <table border="1"><tr><td>PROGRAM ELEMENT NO. 61102F</td><td>PROJECT NO. 2303</td><td>TASK NO. A3</td><td>WORK UNIT ACCESSION NO.</td></tr></table>		PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303	TASK NO. A3	WORK UNIT ACCESSION NO.								
PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303	TASK NO. A3	WORK UNIT ACCESSION NO.												
11. TITLE (Include Security Classification) Raman Study of Solid State Reactions															
12. PERSONAL AUTHOR(S) Dr. Paras N. Prasad															
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 31 Aug 1980	15. PAGE COUNT 10												
16. SUPPLEMENTARY NOTATION															
17. COSATI CODES <table border="1"><tr><th>FIELD</th><th>GROUP</th><th>SUB-GROUP</th></tr><tr><td> </td><td> </td><td> </td></tr><tr><td> </td><td> </td><td> </td></tr><tr><td> </td><td> </td><td> </td></tr></table>		FIELD	GROUP	SUB-GROUP										18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP													
19. ABSTRACT (Continue on reverse if necessary and identify by block number)															
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION unclassified													
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Donald Ball		22b. TELEPHONE (Include Area Code) 767-4960	22c. OFFICE SYMBOL NC												

DTIC
ELECTE
APR 26 1989
S H D

89 4 25 023

AFOSR-TR- 89-0503

FINAL REPORT

PROJECT: RAMAN STUDY OF SOLID STATE REACTIONS

SPONSOR: AFOSR

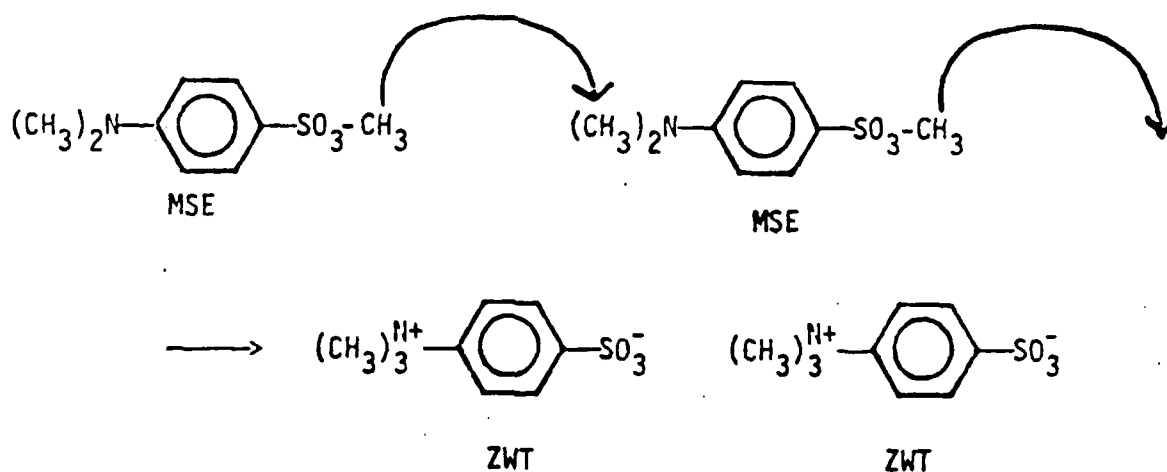
PERIOD: September 1, 1979 to August 31, 1980

CONTRACT #: F49620-79-C-0229

PRINCIPAL INVESTIGATOR: Dr. Paras N. Prasad
Associate Professor
Department of Chemistry
State University of New York at
Buffalo
Buffalo, New York 14214

-1-

The mechanisms and the reaction dynamics of several solid state reactions were investigated. The thermal rearrangement reaction of methyl-p-dimethylaminobenzene sulfonate (MSE) in pure crystal to form the product p-trimethylammonium benzene sulfonate Zwitterion (ZWT) was investigated during this period. Detailed studies of the phonon spectra as well as the internal vibration spectra were made as a function of the percentage rearrangement using polycrystalline samples as well as single crystals in different orientations. Figure 1 shows the spectra for the reactant (top Spectrum), the 40% conversion sample (middle spectrum) and the product (bottom spectrum) for the phonon region. Except for the spectral intensity changes due to a difference in orientation, the spectra of the 40% conversion sample can be explained as consisting of unperturbed bands of both the reactant and the product. The same is true for samples of other percentage conversion. From this result we conclude that no solid solution between the reactant and the product is formed when the reaction proceeds. In other words the reaction proceeds by a heterogeneous mechanism. This observation is consistent with the following mechanism:



1



by _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

This mechanism involves an intermolecular transfer of methyl group and, thus, a cooperative rearrangement. When the reaction is induced, it has to occur cooperatively over a large domain, and not just locally.

A temperature dependence study of phonons in MSE shown in Figure 2 reveals that phonon transitions broaden rapidly as the temperature is raised from 120°K. There is a low lying phonon at $\sim 27\text{cm}^{-1}$ ($\sim 120^\circ\text{K}$ value, indicated in the figure by an arrow). As the sample is warmed from 120°K, this phonon shifts to lower frequencies and rapidly broadens. By 200°K, this transition cannot be distinguished from the Rayleigh background. From this result we conclude that the low lying phonon of MSE represents an over-damped soft mode which, by executing very large oscillations, may be responsible for inducing the thermal rearrangement reaction. This result, again, lends support to a model based on phonon participation in solid state reactions. Our findings on MSE rearrangement reaction were presented at two conferences:

- (a) American Chemical Society Symposium on April 2, 1979 in Honolulu;
- (b) Molecular Spectroscopy Symposium in June 1979 at Columbus, Ohio.

A paper presenting these results has been published in the Journal of American Chemical Society.

→ Solid state photodimerization of two modifications of trans-cinnamic acids in pure crystals was investigated. The Raman spectra of both the phonon region and the internal vibration region were studied as a function of photodimerization. Figure 3 shows the Raman spectra in phonon region of the trans-cinnamic acids and their respective dimers. In this photodimerization we investigated using the phonon spectra, the mechanism of the product lattice formation, i.e. whether the reaction

0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99

proceeds by a homogeneous mechanism with the formation of a solid solution between the reactant and the product or by a heterogeneous reaction where the product forms its own lattice.

As was suggested in the proposal, phonon spectra proved to be conclusive and it was found that the photodimerization proceeds by a heterogeneous mechanism, i.e. no solid solution forms between the reactant and the product. The major thrust of the research has been to derive a dynamical concept of reactivity by considering the role of phonon motions of the lattice in determining reactivity. Large amplitude phonon motions are the analogs of molecular collisions in the gas phase. The two crystalline modifications of trans-cinnamic acid differ in the degree of reactivity. The β -form is more reactive than the α -form. It can be seen from Figure 3 that the β -form has a very low lying phonon transition ($\sim 27 \text{ cm}^{-1}$) where as for the α -form the lowest phonon transition is at $\sim 52 \text{ cm}^{-1}$. In the 27 cm^{-1} motion the molecules execute large amplitude oscillations which may account for enhanced reactivity. These findings on trans-cinnamic acid were presented at the American Chemical Society Symposium on April 2, 1979 in Honolulu.

Also, the topotactic transformation reaction of iodobenzoyl peroxide was investigated. This reaction is thermally enhanced and yields a number of products. The reaction is topotactic, which involves an oriented growth of the product lattice. This reaction was also found to proceed by a heterogeneous mechanism. A manuscript reporting this work is under preparation. Vibrational spectra of several host matrices were also investigated. The spectra of β -cyclodextrin and tri-o-thymotide

copy
Pg. 4

were obtained. Some preliminary work was also done on the photopolymerization of 2,5-distyryl pyrazine.

An important aspect of a dynamical model is to determine specificity in phonon induction of solid state reactions. In order that a large population of selective and coherent vibrational excitation can be achieved to study its effect on reactivity it is necessary that vibrational relaxation be slow. For this reason it is important to investigate and characterize vibrational relaxation and dephasing in organic solids. This study was undertaken during the tenure of the Air Force contract. Two proto systems were investigated. The dephasing of a localized internal vibration of the naphthalene crystal was investigated by studying the temperature dependence of the line width, the line shape and the line frequency. It was found that at liquid helium temperatures the contribution to dephasing due to physical processes which are of interest to us is almost negligible. The observed dephasing can entirely be explained due to inhomogeneities. Even at higher temperatures the T_1 -relaxation time which is responsible for decay of the vibrational excitation is very long. This result is extremely encouraging from the point of view of being able to selectively pump a high degree of vibrational excitation of a given mode. Another system in which we have studied vibrational relaxation is p-bromochlorobenzene. This system in crystalline state exhibits orientational disorder and our motivation was to study phonon relaxation in a structurally disordered system. The work revealed that even in a structurally disordered system for which both anharmonic interactions and structural disorder provide scattering mechanisms, the study

(100)

of temperature dependence of linewidths can be used to derive information on phonon relaxations. To discern the effect of disorder, the result on p-bromochlorobenzene was also compared with that on isomorphous p-dichlorobenzene crystal which exhibits no structural disorder. It was found that for both these p-dihalobenzenes the phonon relaxation at liquid helium temperatures is $>10^{-10}$ sec.

On the side of the instrumentation progress has also been made. An automation system has been introduced in which experiments are controlled by a Micronova computer. The data are obtained and digitally processed. For larger computations the data can be transferred from Micronova to the University computing facility through a modem. Micronova also controls the multichannel vidicon detection system for time-resolved studies. To improve the signal to noise ratio in this multichannel detection we made several modifications. An iodine filter was assembled which can be used with the $5145\overset{\circ}{\text{Å}}$ laser excitation to reduce the background. We are also in the process of building a background rejection optical-filter for cases where we need to use other excitation wavelengths. This filter consists of two gratings which are put together in a subtractive mode. The first grating disperses the scattered radiation. A stopper in the path of the dispersed beam blocks the laser light and the shorter wavelengths, but passes all the longer wavelengths which then are combined by the second grating and focused on the slit of the 14018 double monochromator. For time-resolved studies which would utilize nanosecond u.v. pulses a nitrogen laser has been built and is currently operative.

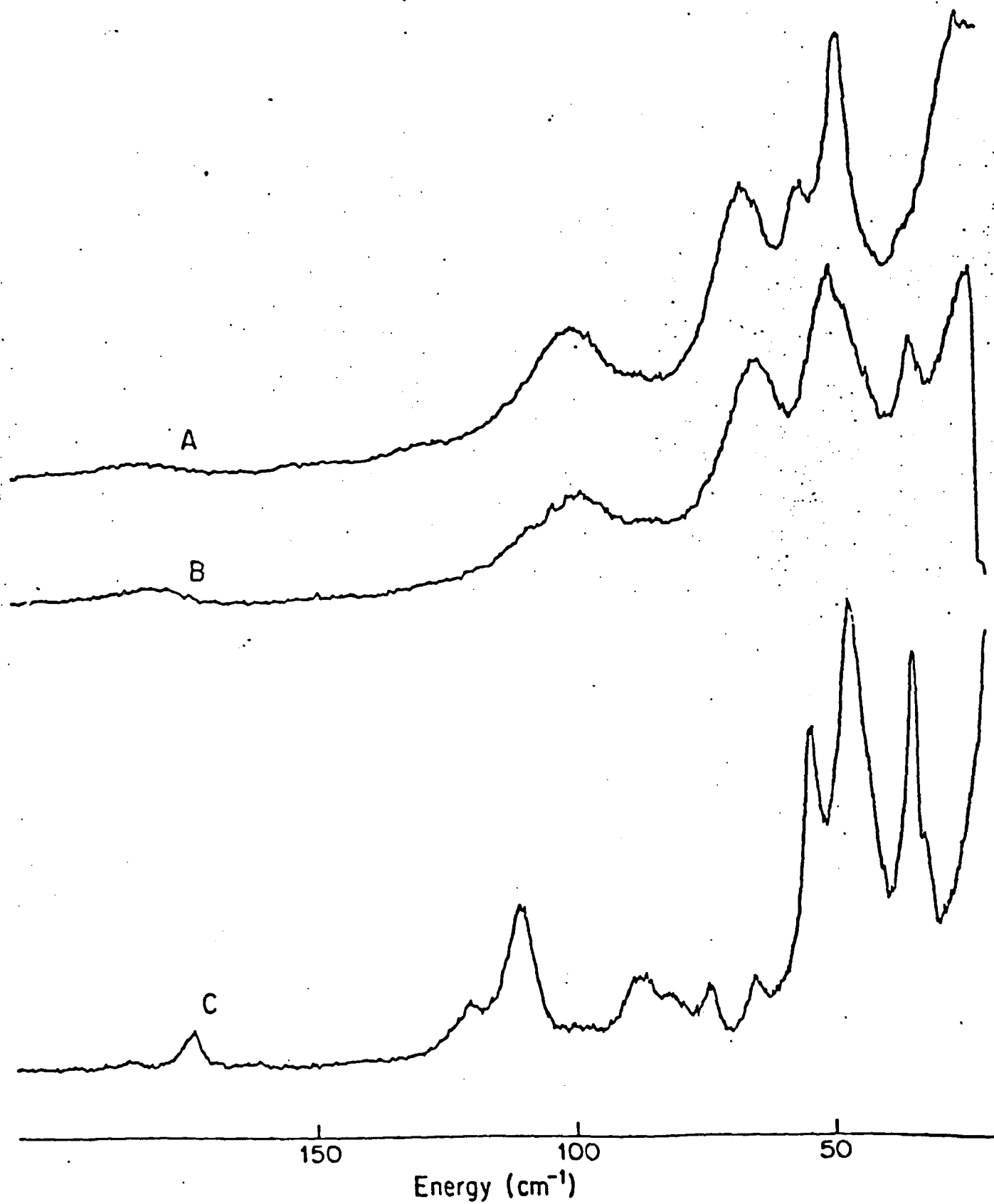


Figure 1

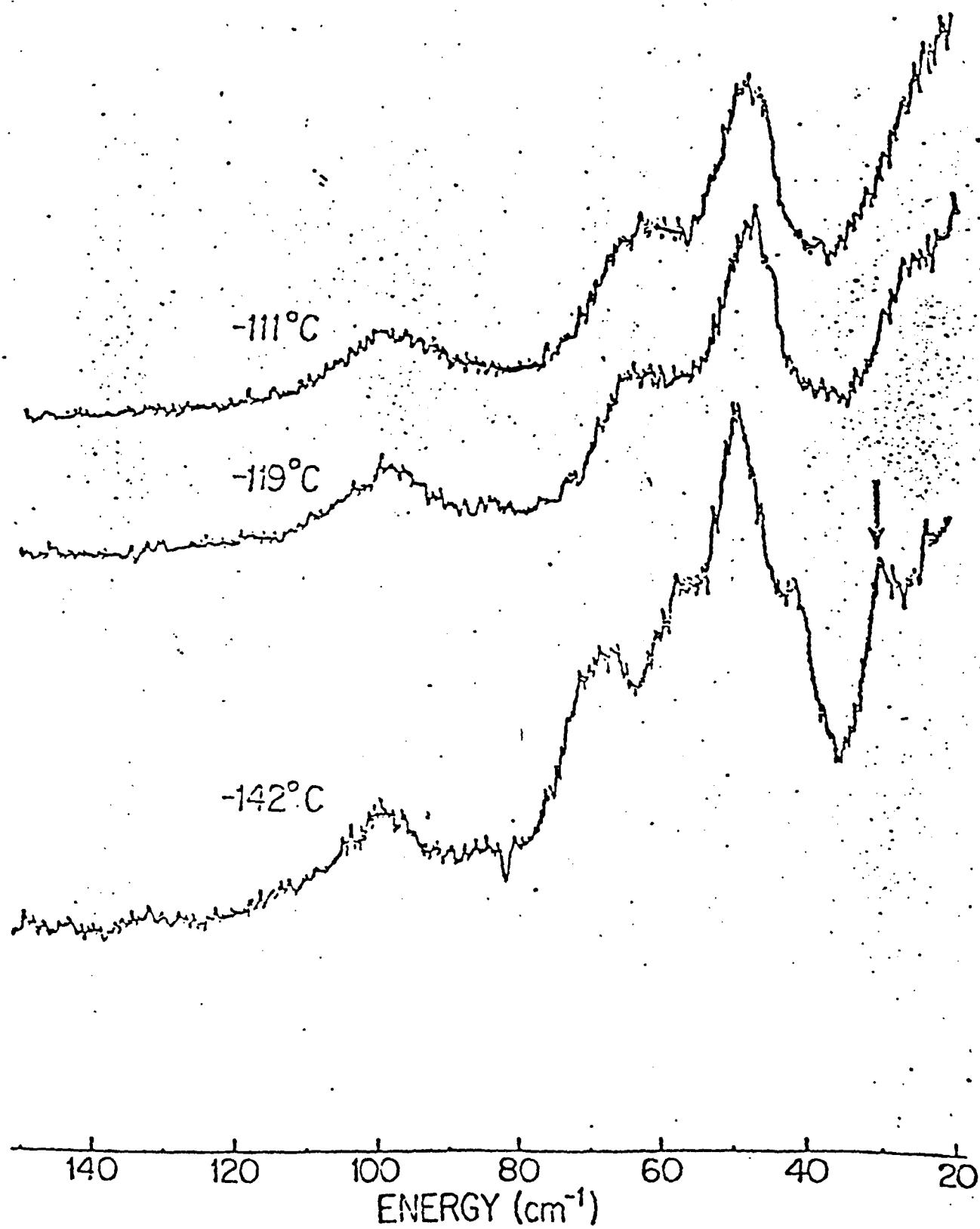
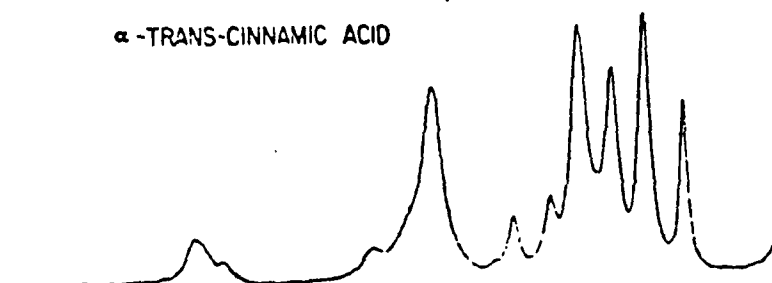


Figure 2

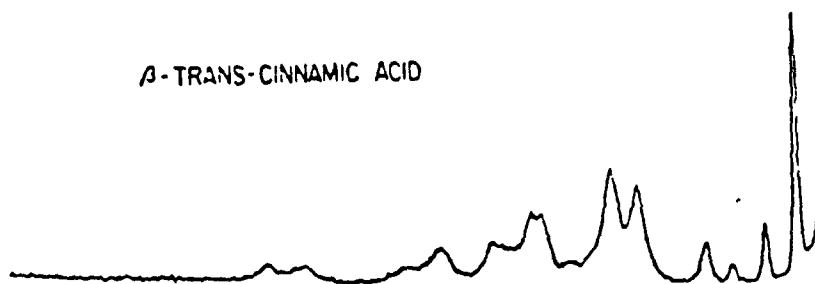
α -TRUXILLIC ACID



α -TRANS-CINNAMIC ACID



β -TRANS-CINNAMIC ACID



β -TRUXINIC ACID

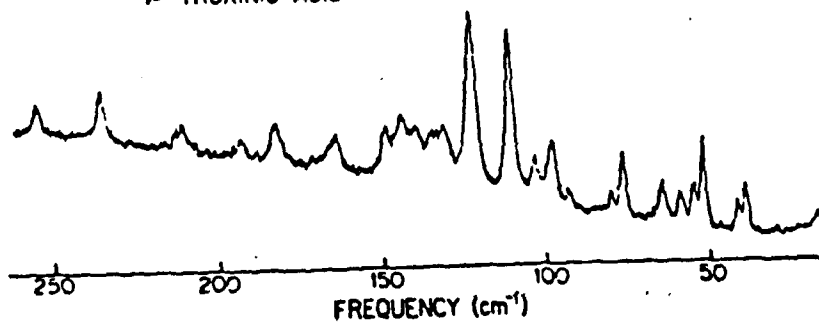


Figure 3

REPORTS OF THE ACCOMPLISHED RESEARCH UNDER AFOSR SUPPORT

PUBLICATIONS

1. "Vibrational Relaxation in a Structurally Disordered Solid: Temperature Dependence of Raman Active Phonons in p-Bromochlorobenzene and p-Dichlorobenzene," P. N. Prasad, and R. V. Smith, J. Chem. Phys. 71, 4646 (1979).
2. "Vibrational Dephasing in Organic Solids: Temperature Dependence of a Localized Raman Active Internal Mode of Naphthalene," L. A. Hess and P. N. Prasad, J. Chem. Phys. 72, 573 (1980).
3. "Vibrational Relaxations and Dephasing in Organic Solids," P. N. Prasad. Mol. Cryst. Liq. Cryst. 58, 39 (1980).
4. "Raman Phonon Spectroscopy of Solid State Reactions: Thermal Rearrangement of Methyl-p-Dimethylaminobenzene Sulfonate in Solid State," K. Dwarakanath and P. N. Prasad, J. Am. Chem. Soc. 102, 4254 (1980).
5. "Structure and Dynamics of the Iodine Column in the Polyiodine Canal Complexes (Benzophenone)₉ (KI)₂I₇CHCl₃" B. A. Bolton, P. Leung, P. Coppens and P. N. Prasad, Manuscript under preparation.

ORAL PRESENTATIONS:

1. "Laser Raman Study of Solid State Reactions," P. N. Prasad. Presented on April 2, 1979 at the American Chemical Society Symposium in Honolulu.
2. "Laser Raman Study of the Thermal Rearrangement of Methyl p-Dimethyl-Aminobenzene Sulfonate in Solid State," K. Dwarakanath, R. V. Smith and P. N. Prasad, Molecular Spectroscopy Symposium, June 12, 1979 at Columbus, Ohio.
3. "Vibrational Relaxation and Dephasing of Raman Active Modes in Molecular Solids and Crystalline Molecular Complexes," L. A. Hess and P. N. Prasad, Molecular Spectroscopy Symposium, June 12, 1979 at Columbus, Ohio.
4. "Dephasing of Optical Excitations in Disordered Organic Solids," L. A. Hess and P. N. Prasad, Molecular Spectroscopy Symposium, June 16, 1980 at Columbus, Ohio.
5. "Raman Study of Solid State Reactions," G. Eisenhardt and P. N. Prasad, Molecular Spectroscopy Symposium, June 14, 1980 at Columbus, Ohio.